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- (73) Proprietor: **DAICEL CHEMICAL INDUSTRIES CO., LTD.**  
1-banchi, Teppo-cho  
Sakai-shi Osaka 590(JP)

- (72) Inventor: **Kanno, Tatsuya**  
500, Kamiyobe Yobe-ku  
Himeji-shi Hyogo(JP)  
Inventor: **Takahashi, Ikuo**  
940, Shinzaike Aboshi-ku  
Himeji-shi Hyogo(JP)  
Inventor: **Sasaki, Kenichi**  
940, Shinzaike Aboshi-ku  
Himeji-shi Hyogo(JP)  
Inventor: **Habe, Tsuyoshi**  
940, Shinzaike Aboshi-ku  
Himeji-shi Hyogo(JP)  
Inventor: **Sei, Tsuyoshi**  
500, Kamiyobe Yobe-ku  
Himeji-shi Hyogo(JP)

- (74) Representative: **Patentanwälte Grünecker, Kinkeldey, Stockmair & Partner**  
Maximilianstrasse 58  
W-8000 München 22(DE)

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## Description

The present invention relates to an aromatic polycarbonate copolymer usable in an optical information recording disk in which signals are recorded by means of a laser beam or recorded signals are read by utilizing the reflecting or transmission of the laser beam.

A high recording density can be provided by an information recording/reproduction system of the DRAW type or Erasable-DRAW-type in which a spot laser beam is applied to a disk to record signals on the disk by means of minute pits or the signals thus recorded by means of such pits are read by detecting the quantity of the reflected or transmitted laser beam.

Particularly in the system of the Erasable-DRAW-type, the record can be erased or written and images and sounds reproduced therefrom are excellent. Thus, it is expected to employ the system of the Erasable-DRAW-type broadly in the recording of images and sounds or reproduction of them and in the recording/reproduction of a large quantity of information. The disk used in the recording/reproduction system does not only have to be transparent so as to transmit the laser beam through the disk body but also optically uniform so as to minimize an error in the readout. When the laser beam is transmitted through the disk body, double refraction occurs due to mainly a thermal stress caused in the cooling and flowing steps of a resin in the molding to form the disk body, molecular orientation and residual stress caused by a change in volume around a glass transition point. A high optical ununiformity due to the double refraction is a fatal defect of optical disks.

The double refraction of the disk occurring mainly due to the thermal stress caused in the cooling and flowing steps of a resin in the molding to form the disk body, molecular orientation and residual stress can be reduced considerably by suitably selecting the molding conditions. However, it still depends greatly on the intrinsic double refraction, i.e. photoelasticity constant, of the molden resin per se.

The double refraction can be represented as the product of the photoelasticity constant and residual stress according to the following formula (1):

$$n_1 - n_2 = C (\sigma_1 - \sigma_2) \quad (1)$$

wherein:

$n_1 - n_2$  represents a double refraction,  
 $\sigma_1 - \sigma_2$  represents a residual stress, and  
 C represents a photoelasticity constant.

It is apparent that the double refraction of the obtained disk can be reduced by reducing the photoelasticity constant in the above formula (1) even when the molding conditions are unchanged.

EP-A-175 905 discloses a statistical copolycarbonate having units derived from 2,2-bis-(4-hydroxy-3-tertiary-butylphenyl)propane and bisphenol A.

EP-A-89 801 discloses that a certain group of substituted aromatic polycarbonates is suitable for the preparation of optical elements.

It is the object of the present invention to provide resins having a low photoelasticity constant and an optical disc containing same as substrates.

Said objects are achieved by an aromatic polycarbonate copolymer composed of 1 to 99 mole percent of the unit of 2,2-bis(4-hydroxy-3-tertiary-butyl-phenyl)-propane, 99 to 1 mole percent of the unit of a comonomer selected from the group consisting of

- (1) 2,2-bis(4-hydroxy-3-methylphenyl)-propane,
  - (2) 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene,
  - (3) 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene,
  - (4) 2,2-bis(4-hydroxyphenyl)-octane and
  - (5) 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)-propane
- and a carbonate group located between the two units.

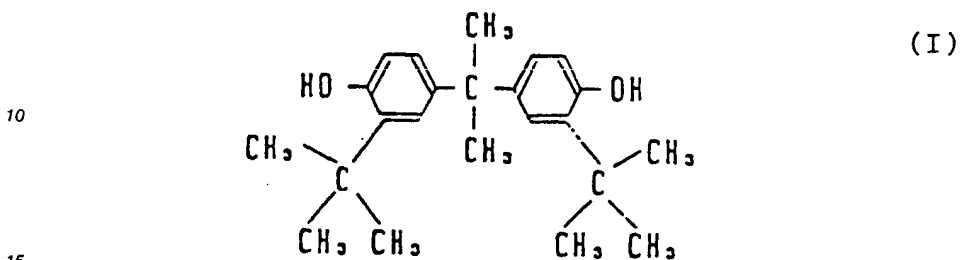
The aromatic polycarbonate copolymer of the invention can be obtained from the first monomer and the comonomer by a carbonate linkage between them.

It is preferred that the comonomer is selected from the group consisting of (1), (2) and (3). The copolymer is composed of 5 to 95 mole percent of the unit of 2,2-bis-(4-hydroxy-3-tertiary-butylphenyl)-propane, 95 to 5 mole percent of the unit of a comonomer selected from the group consisting of (2) and (3) and a carbonate group located between the two units; and the copolymer is composed of 3 to 97 mole percent of the unit of 2,2-bis(4-hydroxy-3-tertiary-butylphenyl)-propane, 97 to 3 mole percent of the unit of a comonomer selected from the group consisting of (4) and (5) and a carbonate group located between the two units.

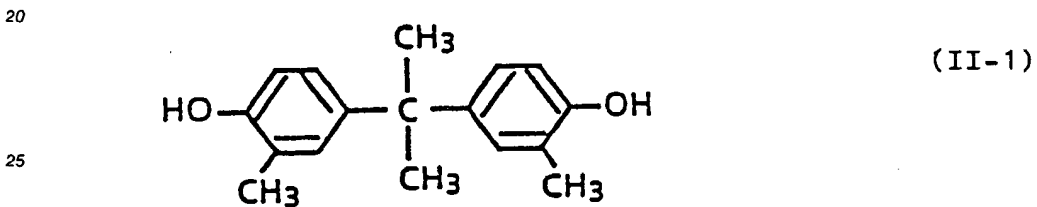
The invention further provides an optical disk which comprises a substrate of the copolymer as defined above and a recording layer coated thereon.

It is preferred that the copolymer for use as the substrate has a viscosity-average molecular weight of 13,000 to 50,000.

5 The first monomer has the formula (I):



The comonomers have the formulas (II-1 to II-5):



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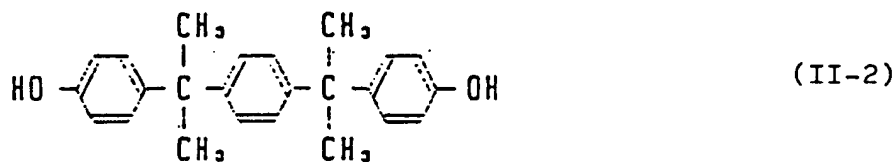
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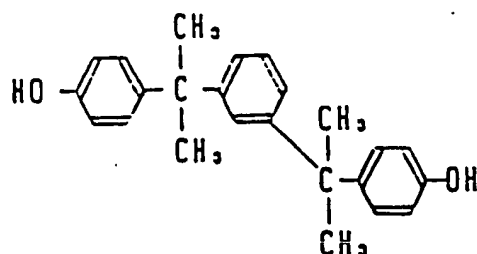
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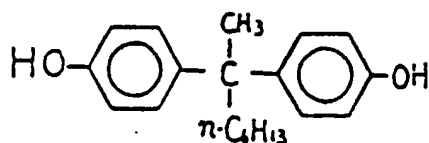
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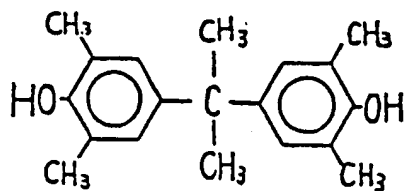




(II-3)



(II-4)



(II-5)

50 The copolymer of the invention has the above defined proportions of the two constituent monomers. If the monomer (I) amounts to less than 5 mole percent, the copolymer has almost the same photoelasticity constant as the homopolycarbonate of the monomer (II). If it amounts to more than 95 mole percent, the copolymer has a much lower glass transition point than the homopolycarbonate of the monomer (II).

55 The copolymer of the present invention has a viscosity-average molecular weight of preferably 1,000 to 100,000 and more preferably 13,000 to 50,000. When this value is less than 1,000, the produced moldings are brittle and, on the contrary, when it exceeds 100,000, the fluidity is lowered to reduce the moldability thereof. Thus, the resin having a viscosity-average molecular weight of less than 1,000 or higher than 100,000 is unsuitable for use as the starting material for the optical disks.

The polycarbonate copolymer of the invention may further comprise a third monomer unit in addition to the above shown essential two monomer units. Said third monomer may be any compound capable of being bonded through the carbonate linkage. The amount (weight ratio) of the third component is not limited so far as it does not impair the physical properties of the product.

5 The polycarbonate copolymer of the present invention can be prepared by the two following processes:

(1) transesterification process:

The two monomers are reacted with each other in the presence of diphenyl carbonate in an amount  
10 slightly larger than its stoichiometric amount and an ordinary carbonation catalyst at a temperature of about 160 to 180°C under atmospheric pressure for about 30 min while an inert gas is introduced thereto. Then, the pressure is gradually reduced over 2 h to finally 1333 Pa (10 Torr) at about 180 to 220°C to complete the precondensation reaction at 220°C. Then the reaction is continued at 270°C under 1333 Pa (10 Torr) for 30 min and then at 270°C under 666,5 Pa (5 Torr) for 20 min. Thereafter the postcondensation reaction  
15 is conducted at 270°C under a reduced pressure of lower than 66,7 Pa (0.5 Torr), preferably 40,0 to 13,3 Pa (0.3 to 0.1 Torr), for 1.5 to 2.0 h.

Suitable carbonation catalysts used for forming the carbonate linkage include alkali metal and alkaline earth metal catalysts such as lithium, potassium, sodium, calcium and tin catalysts. Examples of them include lithium hydroxide, lithium carbonate, potassium borohydride, potassium hydrogenphosphate, sodium  
20 hydroxide, sodium borohydride, calcium hydride, dibutyltin oxide and stannous oxide. Among them, the potassium catalysts are preferred.

(2) Phosgene process:

A three-necked flask is provided with a stirrer, thermometer, gas-inlet tube and gas-outlet tube. A mixture of the two monomers is dissolved in a solvent such as pyridine or dichloromethane and gaseous phosgene is introduced thereto under vigorous stirring. This operation is conducted in a powerful draft chamber, since phosgene is virulent. A unit for decomposing excess phosgene into nonpoisonous compounds with a 10% aqueous sodium hydroxide solution is provided at an end of the outlet tube. Phosgene  
30 is introduced from a bomb into the flask through an empty gas washing bottle, a gas washing bottle containing paraffin (to count the number of bubbles) and an empty gas washing bottle sequentially. The gas inlet tube is inserted into the flask and placed above the stirrer and the end thereof is widened like a funnel so that it is not clogged by the formed pyridine salt.

As the gas is introduced into the flask, pyridine hydrochloride is precipitated and the reaction mixture  
35 becomes turbid. The reaction mixture is cooled with water to keep the reaction temperature below 30°C. As the condensation reaction proceeds, the reaction mixture becomes viscous. Phosgene is introduced thereto until the yellow color of the phosgene/hydrogen chloride complex no more disappears. After completion of the reaction, methanol is added to precipitate the polymer, which is filtered and dried. The polycarbonate thus formed, being soluble for example in methylene chloride, pyridine, chloroform or tetrahydrofuran, is  
40 dissolved therein and reprecipitated from methanol to purify same.

The aromatic polycarbonate of the invention is useful as a starting material for an optical disk to record information. The disk according to the invention includes the direct read after write type (DRAW) and the erasable direct read after write type (Erasable DRAW) and serves to record signals with a laser beam and read recorded signals with reflection or transmission of a laser beam.

45 From the practical point of view, the polycarbonate is used as a supporting substrate for a recording layer. A disk of it is covered with a recording layer such as evaporated metals to form a recording medium. Two recording disks obtained by this way are assembled into one body, for example by bonding with an adhesive or melting and bonding with the ultrasonic waves, through a spacer so that the two recording surfaces may be faced to each other. The recording layer may be further covered with a protective layer.

50 The polycarbonate copolymer of the present invention having a low photoelasticity constant can be used as a starting material for optical information recording disks wherein signals are recorded by a laser beam or recorded signals are read by utilizing the reflection or transmission of the laser beam.

The figures show IR spectra and NMR spectra of the copolymers obtained in the examples, IR spectra odd-numbered, NMR spectra even-numbered.

55 Figs 1 and 2 show those of Example 1,  
Figs 3 and 4 those of Example 3,  
Figs 5 and 6 those of Example 5,  
Figs 7 and 8 those of Example 7,

Figs 9 and 10        those of Example 9,  
 Figs 11 and 12       those of Example 11,  
 Figs 13 and 14       those of Example 13,  
 Figs 15 and 16       those of Example 15, and  
 5 Figs 17 and 18       those of Example 17.

The following examples further illustrate the present invention.  
 In the examples, parts and percentages are given by weight.

#### Example 1

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277 parts (90 mol %) of 2,2-bis-(4-hydroxy-3-methylphenyl)propane, 41 parts (10 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane and 264 parts of diphenyl carbonate were placed in a 3-l three-necked flask. After repeating degassing and nitrogen purge five times, the mixture was molten at 160°C in a silicone bath while nitrogen was introduced thereto. A solution of potassium borohydride (carbonation catalyst) in phenol prepared previously was added to the melt in an amount of  $10^{-3}$  mol % based on the total amount of the bisphenol fed. After aging under stirring at 160°C in a nitrogen atmosphere for 30 min, the pressure was reduced to 13330 Pa (100 Torr) at that temperature and the mixture was stirred for 30 min. Further the pressure was reduced to 6665 Pa (50 Torr) at that temperature and the reaction was continued for additional 30 min. The temperature was elevated slowly to 220°C and the reaction was conducted for 60 min to distill phenol in an amount of 80% based on the theoretical amount. Then the pressure was reduced to 1330 Pa (10 Torr) at that temperature and the reaction was conducted for 30 min. The temperature was elevated slowly to 270°C and the reaction was conducted for 30 min. Further the pressure was reduced to 666,5 Pa (5 Torr) at that temperature and the reaction was conducted for 30 min. The precondensation was thus completed and a nearly theoretical amount of phenol was distilled until this step. Thereafter the postcondensation reaction was conducted at that temperature under 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer was taken out and cooled in a nitrogen atmosphere and its solution viscosity was determined using dichloromethane as the solvent at 20°C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 27,000. In its IR spectrum, a characteristic absorption of a carbonate bond was observed at 1750 to 1800  $\text{cm}^{-1}$  (Fig. 1). In its  $^1\text{H-NMR}$  spectrum, absorptions due to hydrogen in the methyl group of a tert-butyl group at 1.36 ppm, hydrogen in the methyl group of propane at 1.68 ppm and a phenyl group at 7.20 to 7.36 ppm were observed (Fig. 2). From the results of the determination with a DSC (differential scanning calorimeter; Perkin-Elmer 2C), it was found that the glass transition point  $T_g$  was 139°C. The photoelasticity constant  $C$  was 60 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ). From the integrated value of the NMR chart, it was confirmed that the polymer was a polycarbonate copolymer comprising 2,2-bis(4-hydroxy-3-methylphenyl)propane and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 9:1. The devices used in the measurement were an IR spectrometer (IR-810; a product of Nippon Bunkô Co.), a  $^1\text{H-NMR}$  device (JNM-MH-100; a product of JEOL, Ltd.) and a DSC [differential scanning calorimeter (Perkin-Elmer 2C)]. The photoelasticity constant was determined with a device made by the present inventors. The photoelasticity constant was determined by applying various tensile stresses to test pieces (50 mm x 10 mm x 1 mm) lengthwise, measuring the double refraction, putting the value in the above-mentioned formula (1) and determining the photoelasticity constant from the gradient. The photoelasticity constant of 2,2-bis(4-hydroxyphenyl)propane polycarbonate was 82 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ).

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#### Example 2

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A three-necked flask was provided with a stirrer, thermometer, gas-inlet tube and gas-outlet tube. 277 parts (90 mol %) of 2,2-bis(4-hydroxy-3-methylphenyl)propane and 41 parts (10 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane were dissolved in a 10% aqueous sodium hydroxide solution. Dichloromethane was added to the solution thus prepared. Gaseous phosgene was introduced thereto under vigorous stirring. Phosgene was introduced from a bomb into the flask through an empty gas washing bottle, a gas washing bottle containing water and an empty gas washing bottle sequentially. The reaction temperature was kept below 25°C with water during the introduction of gaseous phosgene. As the condensation reaction proceeded, the solution became viscous. Phosgene was introduced thereto until the yellow color of the phosgene/hydrogen chloride complex no more disappeared. After completion of the reaction, the reaction solution was poured into methanol, the mixture was filtered and the filtration residue was washed with water. This procedure was repeated. The polycarbonate thus formed in the form of a solution in dichloromethane was reprecipitated from methanol to purify the same. After purification followed by drying, the solution viscosity of the product was determined using dichloromethane as the solvent at

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20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 31,000. From the fact that the results similar to those obtained in Example 1 were obtained by the instrumental analysis conducted in the same manner as in Example 1, the formed polymer was identified as a polycarbonate copolymer comprising 2,2-bis-(4-hydroxy-3-methylphenyl)propane and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 9:1.

### Example 3

154 parts (50 mol %) of 2,2-bis-(4-hydroxy-3-methylphenyl)propane, 204 parts (50 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane and 264 parts of diphenyl carbonate were placed in a 3-l three-necked flask. After repeating degassing and nitrogen purge five times, the mixture was molten at 160 °C in a silicone bath while nitrogen was introduced thereinto. A solution of potassium borohydride (carbonation catalyst) in phenol prepared previously was added to the melt in an amount of  $10^{-3}$  mol % based on the total amount of the bisphenol fed. After aging under stirring at 160 °C in a nitrogen atmosphere for 30 min, the pressure was reduced to 13330 Pa (100 Torr) at that temperature and the mixture was stirred for 30 min. Further the pressure was reduced to 6665 Pa (50 Torr) at that temperature and the reaction was continued for additional 60 min. The temperature was elevated slowly to 220 °C and the reaction was conducted for 60 min. The amount of phenol distilled until this step was 80% based on the theoretical amount. Then the pressure was reduced to 1333 Pa (10 Torr) at that temperature and the reaction was conducted for 30 min. The temperature was elevated slowly to 270 °C and the reaction was conducted for 30 min. Further the pressure was reduced to 666,5 Pa (5 Torr) at that temperature and the reaction was conducted for 30 min. The precondensation was thus completed and a nearly theoretical amount of phenol was distilled until this step. Thereafter the postcondensation reaction was conducted at that temperature under 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer was taken out and cooled in a nitrogen atmosphere and its solution viscosity was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 27,000. In its IR spectrum, a characteristic absorption of a carbonate bond was observed at 1740 to 1810  $\text{cm}^{-1}$  (Fig. 3). In its <sup>1</sup>H-NMR spectrum, absorption due to hydrogen in the methyl group of a tert-butyl group at 1.36 ppm, hydrogen in the methyl group of propane at 1.68 ppm, hydrogen in a methyl group at 2.30 ppm and a phenyl group at 7.20 to 7.40 ppm were observed (Fig. 4). From the results of the determination with DSC, it was understood that the glass transition point  $T_g$  was 120 °C. The photoelasticity constant  $C$  was 40 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ). From the integrated value of the NMR chart, it was confirmed that the polymer was a polycarbonate copolymer comprising 2,2-bis(4-hydroxy-3-methylphenyl)propane and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 1:1.

### Example 4

A three-necked flask was provided with a stirrer, thermometer, gas-inlet tube and gas-outlet tube. 154 parts (50 mol %) of 2,2-bis(4-hydroxy-3-methylphenyl)propane and 204 parts (50 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane were dissolved in a 10% aqueous sodium hydroxide solution. Dichloromethane was added to the solution thus prepared. Gaseous phosgene was introduced thereto under vigorous stirring. Phosgene was introduced from a bomb into the flask through an empty gas washing bottle, a gas washing bottle containing water and an empty gas washing bottle sequentially. The reaction temperature was kept below 25 °C with water during the introduction of gaseous phosgene. As the condensation reaction proceeded, the solution became viscous. Phosgene was introduced thereto until the yellow color of the phosgene/hydrogen chloride complex no more disappeared. After completion of the reaction, the reaction solution was poured into methanol, the mixture was filtered and the filtration residue was washed with water. This procedure was repeated. The polycarbonate thus formed in the form of a solution in dichloromethane was reprecipitated from methanol to purify the same. After purification followed by drying, the solution viscosity of the product was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 29,000. From the fact that results similar to those obtained in Example 3 were obtained by the instrumental analysis conducted in the same manner as in Examples 3, the formed polymer was identified as a polycarbonate copolymer comprising 2,2-bis-(4-hydroxy-3-methylphenyl)propane and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 1:1.

### Example 5



46 parts (15 mol %) of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 347 parts (80 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane and 264 parts of diphenyl carbonate were placed in a 3 l three-necked flask. After repeating degassing and nitrogen purge five times, the mixture was molten at 160 °C in a silicone bath while nitrogen was introduced thereto. A solution of potassium borohydride (carbonation catalyst) in phenol prepared previously was added to the melt in an amount of  $10^{-3}$  mol % based on the total amount of the bisphenol fed. After aging under stirring at 160 °C in a nitrogen atmosphere for 30 min, the pressure was reduced to 13330 Pa (100 Torr) at that temperature and the mixture was stirred for 30 min. Further the pressure was reduced to 6665 Pa (50 Torr) at that temperature and the reaction was continued for additional 60 min. The temperature was elevated slowly to 220 °C and the reaction was conducted for 60 min. The amount of phenol distilled until this step was 80% based on the theoretical amount. Then the pressure was reduced to 1333 Pa (10 Torr) at that temperature and the reaction was conducted for 30 min. The temperature was elevated slowly to 270 °C and the reaction was conducted for 30 min. Further the pressure was reduced to 666,5 Pa (5 Torr) at that temperature and the reaction was conducted for 30 min. The precondensation was thus completed and a nearly theoretical amount of phenol was distilled until this step. Thereafter the postcondensation reaction was conducted at that temperature under 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer was taken out and cooled in a nitrogen atmosphere and its solution viscosity was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 18,000. In its IR spectrum, a characteristic absorption of a carbonate bond was observed at 1740 to 1805  $\text{cm}^{-1}$  (Fig. 5). In its  $^1\text{H-NMR}$  spectrum, absorption due to hydrogen in the methyl group of a tert-butyl group at 1.36 ppm, hydrogen in the methyl group of propane at 1.68 ppm, hydrogen in a methyl group at 2.30 ppm and a phenyl group at 7.20 to 7.30 ppm were observed (Fig. 6). From the results of the determination with DSC, it was found that the glass transition point  $T_g$  was 119 °C. The photoelasticity constant  $C$  was 28 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ). From the integrated value of the NMR chart, it was confirmed that the polymer was a polycarbonate copolymer comprising 2,2-bis(4-hydroxy-3-methylphenyl)propane and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 3:17.

#### Example 6

A three-necked flask was provided with a stirrer, thermometer, gas-inlet tube and gas-outlet tube. 46 parts (15 mol %) of 2,2-bis(4-hydroxy-3-methylphenyl)propane and 347 parts (85 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane were dissolved in a 10% aqueous sodium hydroxide solution. Dichloromethane was added to the solution thus prepared. Gaseous phosgene was introduced therein under vigorous stirring. Phosgene was introduced from a bomb into the flask through an empty gas washing bottle, a gas whashing bottle containing water and an empty gas washing bottle sequentially. The reaction temperature was kept below 25 °C with water during the introduction of gaseous phosgene. As the condensation reaction proceeded, the solution became viscous. Phosgene was introduced thereto until the yellow color of the phosgene/hydrogen chloride complex no more disappeared. After completion of the reaction, the reaction solution was poured into methanol, the mixture was filtered and the filtration residue was washed with water. This procedure was repeated. The polycarbonate thus formed in the form of a solution in dichloromethane was reprecipitated from methanol to purity same. After purification followed by drying, the solution viscosity of the product was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 20,000. From the fact that results similar to those obtained in Example 5 were obtained by the instrumental analysis conducted in the same manner as in Example 5, the formed polymer was identified as a polycarbonate copolymer comprising 2,2-bis(4-hydroxy-3-methylphenyl)propane and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 3:17.

#### Example 7

374 parts (90 mol %) of 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene, 41 parts (10 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane and 264 parts of diphenyl carbonate were placed in a 3 l three-necked flask. After repeating degassing and nitrogen purge five times, the mixture was molten at 160 °C in a silicone bath while nitrogen was introduced therein. A solution of potassium borohydride (carbonation catalyst) in phenol prepared previously was added to the melt in an amount of  $10^{-3}$  mol % based on the total amount of the bisphenol fed. After aging under stirring at 160 °C in a nitrogen atmosphere for 30 min, the pressure was reduced to 13330 Pa (100 Torr) at that temperature and the mixture was stirred for 30 min. Further the pressure was reduced to 6665 Pa (50 Torr) at that temperature and the reaction was

continued for additional 30 min. The temperature was elevated slowly to 220°C and the reaction was conducted for 60 min to distill phenol in an amount of 80 % based on the theoretical amount. Then the pressure was reduced to 1333 Pa (10 Torr) at that temperature and the reaction was conducted for 30 min. The temperature was elevated slowly to 270°C and the reaction was conducted for 30 min. Further the pressure was reduced to 666,5 (5 Torr) at that temperature and the reaction was conducted for 30 min. The precondensation was thus completed and a nearly theoretical amount of phenol was distilled until this step. Thereafter the postcondensation reaction was conducted at that temperature under 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer was taken out and cooled in a nitrogen atmosphere and its solution viscosity was determined using dichloromethane as the solvent at 20°C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 24,000. In its IR spectrum, a characteristic absorption of a carbonate bond was observed at 1720 to 1820  $\text{cm}^{-1}$  (Fig. 7). In its  $^1\text{H-NMR}$  spectrum, absorptions of hydrogen in the methyl group of a tert-butyl group at 1.34 and 1.38 ppm, hydrogen of the methyl group of propane at 1.65 and 1.68 ppm and a phenyl group at 7.04 to 7.34 ppm were observed (Fig. 8). From the results of the determination with DSC (differential scanning calorimeter; Perkin-Elmer 2C), it was found that the glass transition point  $T_g$  was 146°C. The photoelasticity constant  $C$  was 56 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ). From the integrated value of the NMR chart, it was confirmed that the polymer was a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 9:1.

The devices used in the measurement were an IR spectrometer (IR-810; a product of Nippon Bunko Co.), a  $^1\text{H-NMR}$  device JNM-GX-270 (a product of JEOL, Ltd.) and a DSC [(differential scanning calorimeter (Perkin-Elmer 2C)]. The photoelasticity constant was determined with a device made by the present inventors. The photoelasticity constant was determined by applying various tensile stresses to test pieces (50 mm x 10 mm x 1 mm) lengthwise, measuring the double refraction, putting the value in the above-mentioned formula (1) and determining the photoelasticity constant from the gradient. The photoelasticity constant of 2,2-bis(4-hydroxyphenyl)propane polycarbonate was 82 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ).

#### Example 8

A three-necked flask was provided with a stirrer, thermometer, gas-inlet tube and gas-outlet tube. 374 parts (90 mol %) of 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene and 41 parts (10 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane were dissolved in a 10 % aqueous sodium hydroxide solution. Dichloromethane was added to the solution thus prepared. Gaseous phosgene was introduced thereinto under vigorous stirring. Phosgene was introduced from a bomb into the flask through an empty gas washing bottle, a gas washing bottle containing water and an empty gas washing bottle sequentially. The reaction temperature was kept below 25°C with water during the introduction of gaseous phosgene. As the condensation reaction proceeded, the solution became viscous. Phosgene was introduced thereinto until the yellow color of the phosgene/hydrogen chloride complex no more disappeared. After completion of the reaction, the reaction solution was poured into methanol, the mixture was filtered and the filtration residue was washed with water. This procedure was repeated. The polycarbonate thus formed in the form of a solution in dichloromethane was reprecipitated from methanol to purify same.

After purification followed by drying, the solution viscosity of the product was determined using dichloromethane as the solvent at 20°C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 29,000. From the fact that results similar to those obtained in Example 7 were obtained by the instrumental analysis conducted in the same manner as in Example 7, the formed polymer was identified as a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 9:1.

#### Example 9

208 parts (50 mol %) of 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene, 204 parts (50 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane and 264 parts of diphenyl carbonate were placed in a 3 l three-necked flask. After repeating degassing and nitrogen purge five times, the mixture was molten at 160°C in a silicone bath while nitrogen was introduced thereto. A solution of potassium borohydride (carbonation catalyst) in phenol prepared previously was added to the melt in an amount of  $10^{-3}$  mol % based on the total amount of the bisphenol fed. After aging under stirring at 160°C in a nitrogen atmosphere for 30 min, the pressure was reduced to 13330 Pa (100 Torr) at that temperature and the mixture was stirred for 30 min. Further the pressure was reduced to 6665 Pa (50 Torr) at that temperature and the reaction was continued for additional 60 min. The temperature was elevated slowly to 220°C and the reaction was

conducted for 60 min. The amount of phenol distilled until this step was 80 % based on the theoretical amount. Then the pressure was reduced to 1333 Pa (10 Torr) at that temperature and the reaction was conducted for 30 min. The temperature was elevated slowly to 270 °C and the reaction was conducted for 30 min. Further the pressure was reduced to 666,5 Pa (5 Torr) at that temperature and the reaction was conducted for 30 min. The precondensation was thus completed and a nearly theoretical amount of phenol was distilled until this step. Thereafter the postcondensation reaction was conducted at that temperature under 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer was taken out and cooled in a nitrogen atmosphere and its solution viscosity was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 25,000. In its IR spectrum, a characteristic absorption of a carbonate bond was observed at 1760 to 1800  $\text{cm}^{-1}$  (Fig. 9). In its  $^1\text{H-NMR}$  spectrum, absorptions of hydrogen in the methyl group of a tert-butyl group at 1.34 and 1.38 ppm, hydrogen in the methyl group of propane at 1.65 and 1.68 ppm and a phenyl group at 7.02 to 7.30 ppm were observed (Fig. 10). From the results of the determination with DSC, it was found that the glass transition point  $T_g$  was 136 °C. The photoelasticity constant  $C$  was 41 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ). From the integrated value of the NMR chart, it was confirmed that the polymer was a polycarbonate comprising 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 1:1.

#### Example 10

A three-necked flask was provided with a stirrer, thermometer, gas-inlet tube and gas-outlet tube. 208 parts (50 mol %) of 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene and 204 parts (50 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane were dissolved in a 10 % aqueous sodium hydroxide solution. Dichloromethane was added to the solution thus prepared. Gaseous phosgene was introduced thereinto under vigorous stirring. Phosgene was introduced from a bomb into the flask through an empty gas-washing bottle, a gas washing bottle containing water and an empty gas washing bottle sequentially. The reaction temperature was kept below 25 °C with water during the introduction of gaseous phosgene. As the condensation reaction proceeded, the solution became viscous. Phosgene was introduced thereinto until the yellow color of the phosgene/hydrogen chloride complex no more disappeared. After completion of the reaction, the reaction solution was poured into methanol, the mixture was filtered and the filtration residue was washed with water. This procedure was repeated. The polycarbonate thus formed in the form of a solution in dichloromethane was reprecipitated from methanol to purify same.

After purification followed by drying, the solution viscosity of the product was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 28,000. From the fact that results similar to those obtained in Example 9 were obtained by the instrumental analysis conducted in the same manner as in Example 9, the formed polymer was identified as a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 1:1.

#### Example 11

63 parts (15 mol %) of 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene, 347 parts (85 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane and 264 parts of diphenyl carbonate were placed in a 3 l three-necked flask. After repeating degassing and nitrogen purge five times, the mixture was molten at 160 °C in a silicone bath while nitrogen was introduced thereto. A solution of potassium borohydride (carbonation catalyst) in phenol prepared previously was added to the melt in an amount of  $10^{-3}$  mol % based on the total amount of the bisphenol fed. After aging under stirring at 160 °C in a nitrogen atmosphere for 30 min, the pressure was reduced to 13330 Pa (100 Torr) at that temperature and the mixture was stirred for 30 min. Further the pressure was reduced to 6665 Pa (50 Torr) at that temperature and the reaction was continued for additional 60 min. The temperature was elevated slowly to 220 °C and the reaction was conducted for 60 min. The amount of phenol distilled until this step was 80 % based on the theoretical amount. Then the pressure was reduced to 1333 Pa (10 Torr) at that temperature and the reaction was conducted for 30 min. The temperature was elevated slowly to 270 °C and the reaction was conducted for 30 min. Further the pressure was reduced to 666,5 Pa (5 Torr) at that temperature and the reaction was conducted for 30 min. The precondensation was thus completed and a nearly theoretical amount of phenol was distilled until this step. Thereafter the postcondensation reaction was conducted at that temperature under 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer was taken out and cooled in a nitrogen atmosphere and its solution viscosity was determined using dichloromethane as the solvent at 20 °C. The

viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 18,000. In its IR spectrum, a characteristic absorption of a carbonate bond was observed at 1710 to 1820  $\text{cm}^{-1}$  (Fig. 11). In its  $^1\text{H-NMR}$  spectrum, absorption of hydrogen in the methyl group of a tert-butyl group at 1.34 and 1.38 ppm, hydrogen of the methyl group of propane at 1.65 and 1.68 ppm and a phenyl group at 7.05 to 7.30 ppm were observed (Fig. 12). From the results of the observation with DSC, it was found that the glass transition point  $T_g$  was 126 °C. The photoelasticity constant  $C$  was 25 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ). From the integrated value of the NMR chart, it was confirmed that the polymer was a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 3:17.

#### 10 Example 12

A three-necked flask was provided with a stirrer, thermometer, gas-inlet tube and gas-outlet tube. 63 parts (15 mol %) of 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene and 347 parts (85 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane were dissolved in a 10 % aqueous sodium hydroxide solution. Dichloromethane was added to the solution thus prepared. Gaseous phosgene was introduced thereto under vigorous stirring. Phosgene was introduced from a bomb into the flask through an empty gas-washing bottle, a gas washing bottle containing water and an empty gas washing bottle sequentially. The reaction temperature was kept below 25 °C with water during the introduction of gaseous phosgene. As the condensation reaction proceeded, the solution became viscous. Phosgene was introduced thereto until the yellow color of the phosgene/hydrogen chloride complex no more disappeared. After completion of the reaction, the reaction solution was poured into methanol, the mixture was filtered and the filtration residue was washed with water. This procedure was repeated. The polycarbonate thus formed in the form of a solution in dichloromethane was reprecipitated from methanol to purify same.

After purification followed by drying, the solution viscosity of the product was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 23,000. From the fact that results similar to those obtained in Example 11 were obtained by the instrumental analysis conducted in the same manner as in Example 11, the formed polymer was identified as a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 3:17.

#### 30 Example 13

374 parts (90 mol %) of 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene, 41 parts (10 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane and 264 parts of diphenyl carbonate were placed in a 3 l three-necked flask. After repeating degassing and nitrogen purge five times, the mixture was molten at 160 °C in a silicone bath while nitrogen was introduced thereto. A solution of potassium borohydride (carbonation catalyst) in phenol prepared previously was added to the melt in an amount of  $10^{-3}$  mol % based on the total amount of the bisphenol fed. After aging under stirring at 160 °C in a nitrogen atmosphere for 30 min, the pressure was reduced to 13330 Pa (100 Torr) at that temperature and the mixture was stirred for 30 min. Further the pressure was reduced to 6665 Pa (50 Torr) at that temperature and the reaction was continued for additional 30 min. The temperature was elevated slowly to 220 °C and the reaction was conducted for 60 min to distill phenol in an amount of 80 % based on the theoretical amount. Then the pressure was reduced to 1333 Pa (10 Torr) at that temperature and the reaction was conducted for 30 min. The temperature was elevated slowly to 270 °C and the reaction was conducted for 30 min. Further the pressure was reduced to 666,5 Pa (5 Torr) at that temperature and the reaction was conducted for 30 min. The precondensation was thus completed and a nearly theoretical amount of phenol was distilled until this step. Thereafter the postcondensation reaction was conducted at that temperature under 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer was taken out and cooled in a nitrogen atmosphere and its solution viscosity was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 25,000. In its IR spectrum, a characteristic absorption of a carbonate bond was observed at 1760 to 1800  $\text{cm}^{-1}$  (Fig. 13). In its  $^1\text{H-NMR}$  spectrum, absorptions of hydrogen in the methyl group of a tert-butyl group at 1.37 ppm, hydrogen in the methyl group of propane at 1.64 ppm and a phenyl group at 6.80 to 7.25 ppm were observed (Fig. 14). From the results of the determination with DSC (differential scanning calorimeter; Perkin-Elmer 2C), it was found that the glass transition point  $T_g$  was 103 °C. The photoelasticity constant  $C$  was 60 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ). From the integrated value of the NMR chart, it was confirmed that the polymer was a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 9:1.

The devices used in the measurement were an IR spectrometer (IR-810; a product of Nippon Bunkô Co.), a  $^1\text{H-NMR}$  device JNM-GX-270 (a product of JEOL, Ltd.) and a DSC [(differential scanning calorimeter (Perkin-Elmer 2C)] The photoelasticity constant was determined with a device made by the present inventors. The photoelasticity constant was determined by applying various tensile stresses to test pieces (50 mm x 10 mm x 1 mm) lengthwise, measuring the double refraction, putting the value in the above-mentioned formula (1) and determining the photoelasticity constant from the gradient. The photoelasticity constant of 2,2-bis(4-hydroxyphenyl)propane polycarbonate was 82 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ).

#### Example 14

A three-necked flask was provided with a stirrer, thermometer, gas-inlet tube and gas-outlet tube. 374 parts (90 mol %) of 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene and 41 parts (10 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane were dissolved in a 10 % aqueous sodium hydroxide solution. Dichloromethane was added to the solution thus prepared. Gaseous phosgene was introduced thereto under vigorous stirring. Phosgene was introduced from a bomb into the flask through an empty gas washing bottle, a gas washing bottle containing water and an empty gas washing bottle sequentially. The reaction temperature was kept below  $25^\circ\text{C}$  with water during the introduction of gaseous phosgene. As the condensation reaction proceeded, the solution became viscous. Phosgene was introduced thereto until the yellow color of the phosgene/hydrogen chloride complex no more disappeared. After completion of the reaction, the reaction solution was poured into methanol, the mixture was filtered and the filtration residue was washed with water. This procedure was repeated. The polycarbonate thus formed in the form of a solution in dichloromethane was reprecipitated from methanol to purify same.

After purification followed by drying, the solution viscosity of the product was determined using dichloromethane as the solvent at  $20^\circ\text{C}$ . The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 27,500. From the fact that results similar to those obtained in Example 13 were obtained by the instrumental analysis conducted in the same manner as in Example 13, the formed polymer was identified as a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 9:1.

#### Example 15

208 parts (50 mol %) 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene, 204 parts (50 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane and 264 parts of diphenyl carbonate were placed in a three-necked flask. After repeating degassing and nitrogen purge five times, the mixture was molten at  $160^\circ\text{C}$  in a silicone bath while nitrogen was introduced therein. A solution of potassium borohydride (carbonation catalyst) in phenol prepared previously was added to the melt in an amount of  $10^{-3}$  mol % based on the total amount of the bisphenol fed. After aging under stirring at  $160^\circ\text{C}$  in a nitrogen atmosphere for 30 min, the pressure was reduced to 13330 Pa (100 Torr) at that temperature and the mixture was stirred for 30 min. Further the pressure was reduced to 6665 Pa (50 Torr) at that temperature and the reaction was continued for additional 60 min. The temperature was elevated slowly to  $220^\circ\text{C}$  and the reaction was conducted for 60 min. The amount of phenol distilled until this step was 80 % based on the theoretical amount. Then the pressure was reduced to 1333 Pa (10 Torr) at that temperature and the reaction was conducted for 30 min. The temperature was elevated slowly to  $270^\circ\text{C}$  and the reaction was conducted for 30 min. Further the pressure was reduced to 666,5 Pa (5 Torr) at that temperature and the reaction was conducted for 30 min. The precondensation was thus completed and a nearly theoretical amount of phenol was distilled until this step. Thereafter the post-condensation reaction was conducted at that temperature under 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer was taken out and cooled in a nitrogen atmosphere and its solution viscosity was determined using dichloromethane as the solvent at  $20^\circ\text{C}$ . The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 25,000. In its IR spectrum, a characteristic absorption of a carbonate bond was observed at  $1750$  to  $1800 \text{ cm}^{-1}$  (Fig. 15). In its  $^1\text{H-NMR}$  spectrum, absorptions of hydrogen in the methyl group of a tert-butyl group at 1.38 ppm, hydrogen in the methyl group of propane at 1.64 and 1.70 ppm and a phenyl group at 6.9 to 7.3 ppm were observed (Fig. 16). From the results of the determination with DSC, it was found that the glass transition point  $T_g$  was  $111^\circ\text{C}$ . The photoelasticity constant  $C$  was 39 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ). From the integrated value of the NMR chart, it was confirmed that the polymer was a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 1:1.

#### Example 16

A three-necked flask was provided with a stirrer, thermometer, gas-inlet tube and gas-outlet tube. 208 parts (50 mol %) of 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene and 204 parts (50 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane were dissolved in a 10 % aqueous sodium hydroxide solution. Dichloromethane was added to the solution thus prepared. Gaseous phosgene was introduced thereto under vigorous stirring. Phosgene was introduced from a bomb into the flask through an empty gas-washing bottle, a gas washing bottle containing water and an empty gas washing bottle sequentially. The reaction temperature was kept below 25 °C with water during the introduction of gaseous phosgene. As the condensation reaction proceeded, the solution became viscous. Phosgene was introduced thereto until the yellow color of the phosgene/hydrogen chloride complex no more disappeared. After completion of the reaction, the reaction solution was poured into methanol, the mixture was filtered and the filtration residue was washed with water. This procedure was repeated. The polycarbonate thus formed in the form of a solution in dichloromethane was reprecipitated from methanol to purify same.

After purification followed by drying, the solution viscosity of the product was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 31,000. From the fact that results similar to those obtained in Example 15 were obtained by the instrumental analysis conducted in the same manner as in Example 15, the formed polymer was identified as a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 1:1.

#### 20 Example 17

63 parts (15 mol %) of 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene, 347 parts (85 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane and 264 parts of diphenyl carbonate were placed in a 3-l three-necked flask. After repeating degassing and nitrogen purge five times, the mixture was molten at 160 °C in a silicone bath while nitrogen was introduced thereto. A solution of potassium borohydride (carbonation catalyst) in phenol prepared previously was added to the melt in an amount of  $10^{-3}$  mol % based on the total amount of the bisphenol fed. After aging under stirring at 160 °C in a nitrogen atmosphere for 30 min, the pressure was reduced to 13330 Pa (100 Torr) at that temperature and the mixture was stirred for 30 min. Further the pressure was reduced to 6665 Pa (50 Torr) at that temperature and the reaction was continued for additional 60 min. The temperature was elevated slowly to 220 °C and the reaction was conducted for 60 min. The amount of phenol distilled until this step was 80 % based on a theoretical amount. Then the pressure was reduced to 1333 Pa (10 Torr) at that temperature and the reaction was conducted for 30 min. The temperature was elevated slowly to 270 °C and the reaction was conducted for 30 min. Further the pressure was reduced to 666,5 Pa (5 Torr) at that temperature and the reaction was conducted for 30 min. The precondensation was thus completed and a nearly theoretical amount of phenol was distilled until this step. Thereafter the postcondensation reaction was conducted at that temperature under 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer was taken out and cooled in a nitrogen atmosphere and its solution viscosity was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 26,700. In its IR spectrum, a characteristic absorption of a carbonate bond was observed at 1720 to 1820  $\text{cm}^{-1}$  (Fig. 17). In its  $^1\text{H-NMR}$  spectrum, absorption of hydrogen in the methyl group of a tert-butyl group at 1.39 ppm, hydrogen of the methyl group of propane at 1.64 and 1.70 ppm and a phenyl group at 6.95 to 7.28 were observed (Fig. 18). From the results of the observation with DSC, it was found that the glass transition point  $T_g$  was 118 °C. The photoelasticity constant  $C$  was 28 Brewsters ( $10^{-12} \text{ m}^2/\text{N}$ ). From the integrated value of the NMR chart, it was confirmed that the polymer was a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 3:17.

#### Example 18

A three-necked flask was provided with a stirrer, thermometer, gas-inlet tube and gas-outlet tube. 63 parts (15 mol %) of 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene and 347 parts (85 mol %) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane were dissolved in a 10 % aqueous sodium hydroxide solution. Dichloromethane was added to the solution thus prepared. Gaseous phosgene was introduced thereto under vigorous stirring. Phosgene was introduced from a bomb into the flask through an empty gas-washing bottle, a gas washing bottle containing water and an empty gas washing bottle sequentially. The reaction temperature was kept below 25 °C with water during the introduction of gaseous phosgene. As the condensation reaction proceeded, the solution became viscous. Phosgene was introduced thereto until the yellow color of the phosgene/hydrogen chloride complex no more disappeared. After completion of the

reaction, the reaction solution was poured into methanol, the mixture was filtered and the filtration residue was washed with water. This procedure was repeated. The polycarbonate thus formed in the form of a solution in dichloromethane was reprecipitated from methanol to purify same.

After purification followed by drying the solution viscosity of the product was determined using dichloromethane as the solvent at 20 °C. The viscosity-average molecular weight  $\bar{M}_v$  calculated from the solution viscosity was 29,500. From the fact that results similar to those obtained in Example 17 were obtained by the instrumental analysis conducted in the same manner as in Example 17, the formed polymer was identified as a polycarbonate copolymer comprising 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene and 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane in a ratio of 3:17.

In the below shown examples, the viscosity-average molecular weight was determined by measurement of an intrinsic viscosity and the below shown formula, corresponding to that of bisphenol-A polycarbonate.  $[\eta] = 1.11 \times 10^{-4} M^{0.82}$  [E. Miller & O. Bayer, U.S.P. 2,999,884 (1961)] which represents the relationship between the molecular weight  $M$  and the intrinsic viscosity  $[\eta]$  of bisphenol-A polycarbonate measured at 20 °C using methylene chloride solution. The photoelasticity constant was obtained by substituting the formula (1) above for varied amounts of tensile stress applied in the longitudinal direction of a sample measuring 50 x 10 x 1 mm.

#### Example 19

A 3 l three-necked flask was charged with 179 parts by weight (50 mol%) of 2,2-bis(4-hydroxyphenyl)-octane, 204 parts by weight (50 mol%) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane, and 264 parts by weight of diphenyl carbonate. Deaeration and purging with a nitrogen gas were each repeated five times. Thereafter, the mixture was molten on a silicone bath at 160 °C while introducing a nitrogen gas thereto. After completion of the melting, a solution prepared by dissolving potassium borohydride as a carbonation catalyst in phenol (in an amount of  $10^{-3}$  mol% based on the total amount of the bisphenols fed) was added to the molten mixture, followed by stirring in a nitrogen atmosphere at 160 °C for 30 min. The mixture was then stirred at the same temperature under a pressure of 13330 Pa (100 Torr) for 30 min and then allowed to react at the same temperature under a pressure of 6665 Pa (50 Torr) for 60 min. The reaction mixture was gradually heated to 220 °C, followed by reaction at that temperature for 60 min. 80% of the theoretical amount of phenol to be distilled was distilled away in the reactions up to this stage. Thereafter, the reaction was allowed to proceed at the same temperature under a reduced pressure of 1333 Pa (10 Torr) for 40 min. The temperature was gradually raised to 270 °C, followed by reaction at that temperature for 30 min. Further, the reaction was allowed to proceed at the same temperature under a reduced pressure of 666,5 Pa (5 Torr) for 30 min, thereby distilling away phenol in an amount substantially corresponding to the theoretical amount of phenol to be distilled. Thus, the step of pre-condensation was completed. Subsequently, the condensation was conducted at the same temperature under a pressure of 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer as a product was taken out in a nitrogen gas atmosphere and allowed to cool. The solution viscosity of the polymer was determined at 20 °C using dichloromethane as a solvent. The viscosity-average molecular weight ( $\bar{M}_v$ ) of the polymer was calculated based on the value thus obtained and found to be 18,000.

#### Example 20

A three-necked flask was provided with a stirrer, a thermometer, a gas inlet tube, and an exhaust tube. 179 parts by weight of 2,2-bis(4-hydroxyphenyl)octane and 204 parts by weight of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propanewere dissolved in dichloromethane. A 10 wt% aqueous solution of sodium hydroxide was added to the resulting solution. A phosgene gas was fed into the solution with vigorous stirring. Phosgene was fed into the flask from a cylinder through an empty scrubbing bottle, a scrubbing bottle containing water and an empty scrubbing bottle in that order. The reaction temperature was kept at 25 °C or below during the supply of phosgene while cooling the flask with water. As the condensation reaction proceeded, the viscosity of the solution was increased. Phosgene was further supplied until the yellow color derived from a phosgene-hydrogen chloride complex disappeared. After completion of the reaction, the reaction mixture was poured into methanol. The mixture was filtered, followed by repetition of washing with water. The polycarbonate thus obtained was reprecipitated from a dichloromethane solution with methanol to allow it to purify. Thereafter, the purified polymer was sufficiently dried. The solution viscosity of the polymer was then determined at 20 °C using dichloromethane as a solvent. The viscosity-average molecular weight ( $\bar{M}_v$ ) of the polymer was calculated based on the value thus obtained and found to be 19,000.

(Evaluation of recording characteristics)

The polycarbonate copolymers as prepared above were each provided with a recording film, followed by evaluation of optical recording characteristics. Specifically, the polycarbonate copolymers as described in Examples 19 and 20 were molded into disk-shaped substrates each having a diameter of 130 mm and a thickness of 1.2 mm with an injection press (Dynamelter; a product of Meiki Co., Ltd.). A 1,000 Å-thick optical magnetic film was formed on the substrates thus obtained with an alloy target composed of  $Tb_{23.5}Fe_{64.2}Co_{12.3}$  (atomic %) in a sputtering device (RF sputtering device; a product of Ulvac Corporation). On the recording film was formed a 1,000 Å-thick protective film composed of inorganic glass as described in Japanese Patent Laid-Open No. 177449/1985 which was filed by the applicant of the present application using the same sputtering device as that described above. The performance of the resulting optical magnetic recording disks were evaluated in terms of CN ratio, BER, and change-in CN ratio at a temperature of 60 °C and an RH of 90%. The results are shown in Table 1.

Table 1

Sample No.	birefringence ( $\Delta n$ and single pass)	CN (dB) (note: 1)	BER (bit error rate)	change in CN after 30 days (%) (note: 2)	Tg (°C)	C
Ex. 19	10	52	$2 \times 10^{-5}$	90	103	48
Ex. 20	10	52	$2 \times 10^{-5}$	90	103	48
Comp. Ex. (note: 3)	20	46	$5 \times 10^{-5}$	85	-	-
Note: (1) CN ratio: determined under the following conditions: writing power, 7 mW ; reading power, 1mW; frequency of carrier, 1 MHz; resolution band width, 30 kHz. (2) change in CN (%): degree of lowering in CN 30 days after initiation of exposure to an atmosphere kept at a temperature of 60 °C and an RH of 90% relative to initial CN ratio. (3) Comp. Ex.: an optical magnetic disk prepared in the same manner as mentioned above, except that a conventional poly carbonate substrate (AD-5503; a product of Teijin Chemicals Ltd.) was used.						

As can be seen from Table 1, the polycarbonate copolymer according to the present invention has a remarkably improved CN ratio by virtue of the lowering in birefringence and is also excellent in durability.

#### Example 21

A 3 l three-necked flask was charged with 102 parts by weight (30 mol%) of 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane, 286 parts by weight (70 mol%) of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane, and 264 parts by weight of diphenyl carbonate. Deaeration and purging with a nitrogen gas were each repeated five times. Thereafter, the mixture was molten on a silicone bath at 160 °C while introducing a nitrogen gas thereto. After completion of the melting, a solution prepared by dissolving potassium borohydride as a carbonation catalyst in phenol (in an amount of  $10^{-3}$  mol% based on the total amount of the bisphenols fed) was added to the molten mixture, followed by stirring in a nitrogen atmosphere at 160 °C for 30 min. The mixture was then stirred at the same temperature under a pressure of 1333 Pa (10 Torr) for 30 min and then allowed to react at the same temperature under a pressure of 6665 Pa (50 Torr) for 60 min. The reaction mixture was gradually heated to 220 °C, followed by reaction at that temperature for 60 min. 80% of the theoretical amount of phenol to be distilled was distilled away in the reactions up to this stage. Thereafter, the reaction was allowed to proceed at the same temperature under a reduced pressure of 1333 Pa (10 Torr) for 60 min. The temperature was gradually raised to 270 °C, followed by reaction at that temperature for 40 min. Further, the reaction was allowed to proceed at the same temperature under a reduced pressure of 666,5 Pa (5 Torr) for 30 min, thereby distilling away phenol in an amount substantially corresponding to the theoretical amount of phenol to be distilled. Thus, the step of pre-condensation was completed. Subsequently, the condensation was conducted at the same temperature under a pressure of 13,3 to 40,0 Pa (0.1 to 0.3 Torr) for 2 h. The resulting polymer as a product was taken out in a nitrogen gas atmosphere and allowed to cool. The solution viscosity of the polymer was determined at 20 °C using dichloromethane as a solvent. The viscosity-average molecular weight ( $\bar{M}_v$ ) of the polymer was calculated based on the value thus obtained and found to be 16,000.



## Example 22

A three-necked flask was provided with a stirrer, a thermometer, a gas inlet tube, and an exhaust tube. 102 parts by weight of 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane and 286 parts by weight of 2,2-bis(4-hydroxy-3-tert-butylphenyl)propane were dissolved in a 10 wt.% aqueous solution of sodium hydroxide. Dichloromethane was added to the resulting solution. A phosgene gas was fed into the solution with vigorous stirring. Phosgene was fed into the flask from a cylinder through an empty scrubbing bottle, a scrubbing bottle containing water and an empty scrubbing bottle in that order. The reaction temperature was kept at 25°C or below during the supply of phosgene while cooling the flask with water. As the condensation reaction proceeded, the viscosity of the solution was increased. After completion of the reaction, the reaction mixture was poured into methanol. The mixture was filtered, followed by repetition of washing with water. The polycarbonate thus obtained was reprecipitated from a dichloromethane solution with methanol to allow it to purify. Thereafter, the purified polymer was sufficiently dried. The solution viscosity of the polymer was then determined at 20°C using dichloromethane as a solvent. The viscosity-average molecular weight ( $\bar{M}_v$ ) of the polymer was calculated based on the value thus obtained and found to be 19,000.

The copolymers obtained in Examples 21 and 22 were examined in the same way as shown for the copolymers of Examples 19 and 20. The results are shown in Table 2.

Table 2

Sample No.	birefringence ( $\Delta n$ single pass)	CN(dB) (note: 1)	BER (bit error rate)	change in CN after 30 days (%) (note: 2)	Tg ( $^{\circ}$ C)	C
Ex. 21	8	53	$5 \times 10^{-6}$	90	144	38
Ex. 22	6	55	$2 \times 10^{-6}$	95	144	38

## Claims

1. An aromatic polycarbonate copolymer composed of 1 to 99 mole percent of the unit of 2,2-bis (4-hydroxy-3-tertiary-butylphenyl)-propane, 99 to 1 mole percent of the unit of a comonomer selected from the group consisting of

- (1) 2,2-bis(4-hydroxy-3-methylphenyl)-propane,
  - (2) 1,1'-bis(4-hydroxyphenyl)-p-diisopropylbenzene,
  - (3) 1,1'-bis(4-hydroxyphenyl)-m-diisopropylbenzene,
  - (4) 2,2-bis(4-hydroxyphenyl) octane and
  - (5) 2,2-bis(3,5-dimethyl-4-hydroxyphenyl) propane
- and a carbonate group located between the two units.
2. The copolymer of claim 1, which is composed of 5 to 95 mole percent of the unit of 2,2-bis(4-hydroxy-3-tertiary-butylphenyl)-propane, 95 to 5 mole percent of the unit of a comonomer selected from the group consisting of (2) and (3) and a carbonate group located between the two units.
  3. The copolymer of claim 1, which is composed of 3 to 97 mole percent of the unit of 2,2-bis(4-hydroxy-3-tertiary-butylphenyl)-propane, 97 to 3 mole percent of the unit of a comonomer selected from the group consisting of (4) and (5) and a carbonate group located between the two units.
  4. The copolymer of claim 1, which has a viscosity-average molecular weight of 1000 to 100,000.
  5. An optical disk which comprises a substrate of the copolymer according to any of claims 1 to 4 and a recording layer coated thereon.
  6. The optical disk of claim 5, in which the copolymer has a viscosity-average molecular weight of 13,000 to 50,000.

#### Patentansprüche

1. Aromatisches Polycarbonatcopolymer, zusammengesetzt aus 1 bis 99 Mol-% der Einheit von 2,2-Bis(4-hydroxy-3-tert.-butylphenyl)propan, 99 bis 1 Mol-% der Einheit eines Comonomers, gewählt aus der Gruppe, bestehend aus
  - (1) 2,2-Bis(4-hydroxy-3-methylphenyl)propan,
  - (2) 1,1'-Bis(4-hydroxyphenyl)-p-diisopropylbenzol,
  - (3) 1,1'-Bis(4-hydroxyphenyl)-m-diisopropylbenzol,
  - (4) 2,2-Bis(4-hydroxyphenyl)octan und
  - (5) 2,2-Bis(3,5-dimethyl-4-hydroxyphenyl)propan,
 und einer zwischen den zwei Einheiten angeordneten Carbonatgruppe.
2. Copolymer nach Anspruch 1, welches aus 5 bis 95 Mol-% der Einheit von 2,2-Bis(4-hydroxy-3-tert.-butylphenyl)propan, 95 bis 5 Mol-% der Einheit eines Comonomers, gewählt aus der Gruppe, bestehend aus (2) und (3), und einer zwischen den zwei Einheiten angeordneten Carbonatgruppe zusammengesetzt ist.
3. Copolymer nach Anspruch 1, welches aus 3 bis 97 Mol-% der Einheit von 2,2-Bis(4-hydroxy-3-tert.-butylphenyl)propan, 97 bis 3 Mol-% der Einheit eines Comonomers, gewählt aus der Gruppe, bestehend aus (4) und (5), und einer zwischen den zwei Einheiten angeordneten Carbonatgruppe zusammengesetzt ist.
4. Copolymer nach Anspruch 1, welches ein viskositätsdurchschnittliches Molekulargewicht von 1000 bis 100000 besitzt.
5. Optische Platte, welche ein Substrat aus dem Copolymer nach einem der Ansprüche 1 bis 4 und eine darauf aufgebrachte Aufzeichnungsschicht umfaßt.
6. Optische Platte nach Anspruch 5, worin das Copolymer ein gewichtsdurchschnittliches Molekulargewicht von 13000 bis 50000 besitzt.

#### Revendications

1. Copolymère de polycarbonate aromatique comprenant de 1 à 99 moles % du motif dérivé du 2,2-bis(4-hydroxy-3-tert-butylphényl)propane, de 99 à 1 moles % du motif dérivé d'un comonomère choisi parmi

- :
- (1) le 2,2-bis(4-hydroxy-3-méthylphényl)-propane,
  - (2) le 1,1'-bis(4-hydroxyphényl)-p-diisopropylbenzène,
  - (3) le 1,1'-bis(4-hydroxyphényl)-m-diisopropylbenzène,
  - 5 (4) le 2,2-bis(4-hydroxyphényl)-octane, et
  - (5) le 2,2-bis(3,5-diméthyl-4-hydroxyphényl)-propane ;
- et un groupe carbonate situé entre les deux motifs.
- 2. Copolymère selon la revendication 1, comprenant de 5 à 95 moles pour cent du motif dérivé du 2,2-bis(4-hydroxy-3-tert-butylphényl)-propane, de 95 à 5 moles pour cent du motif dérivé d'un comonomère choisi parmi les composés (2) et (3), et un groupe carbonate situé entre les deux motifs.
  - 10 3. Copolymère selon la revendication 1, comprenant de 3 à 97 moles pour cent du motif dérivé du 2,2-bis(4-hydroxy-3-tert-butylphényl)-propane, de 97 à 3 moles pour cent du motif dérivé d'un comonomère choisi parmi les composés (4) et (5), et un groupe carbonate situé entre les deux motifs.
  - 15 4. Copolymère selon la revendication 1, ayant un poids moléculaire moyen déterminé d'après mesure de la viscosité, de 1 000 à 100 000.
  - 20 5. Disque optique comprenant un substrat en le copolymère selon l'une quelconque des revendications 1 à 4, et une couche d'enregistrement déposée sur celui-ci.
  - 6. Disque optique selon la revendication 5, dans lequel le copolymère a un poids moléculaire moyen déterminé d'après mesure de la viscosité, de 13 000 à 50 000.

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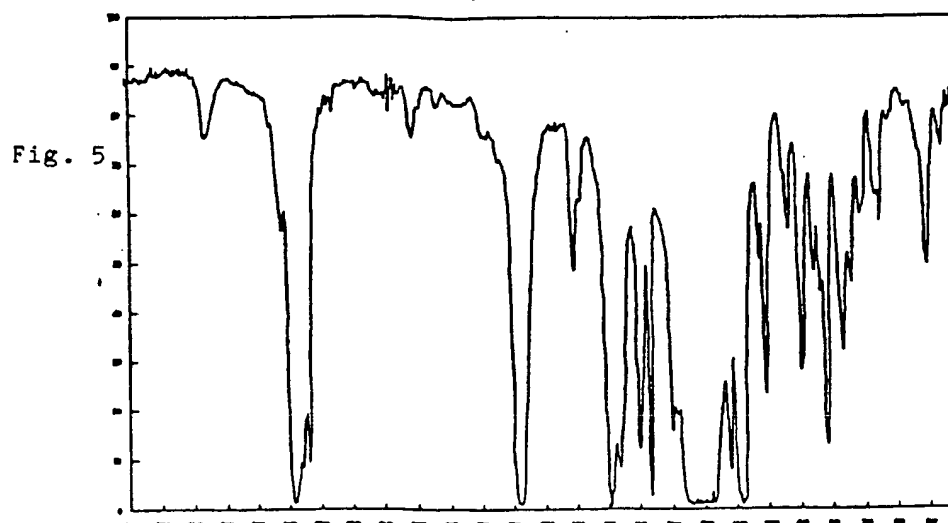
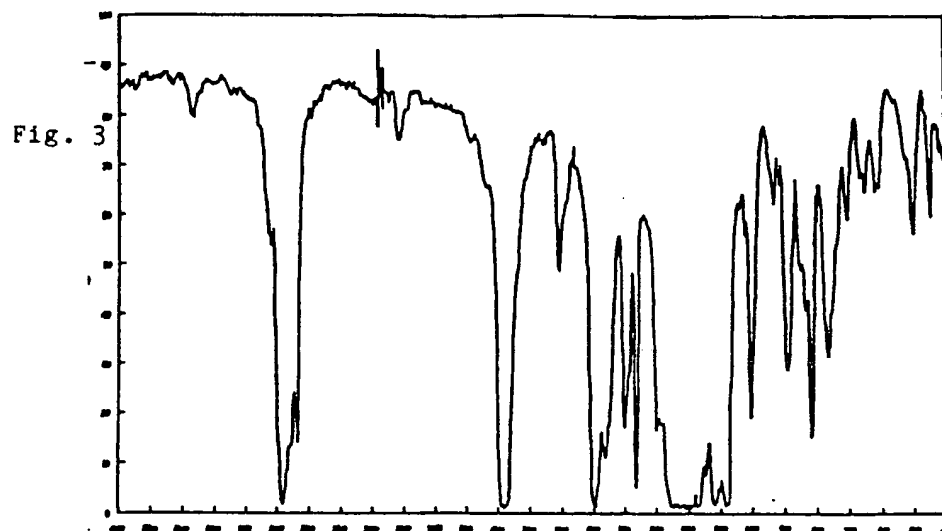
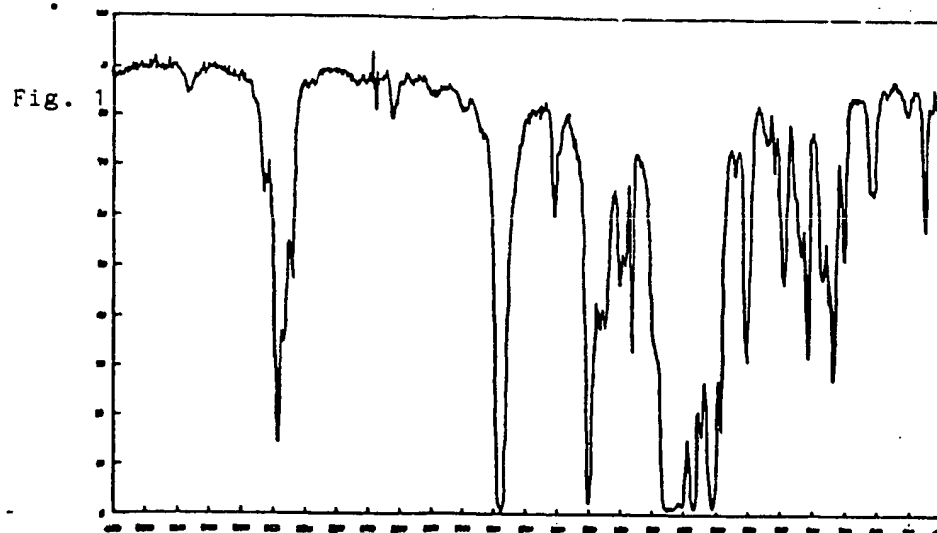


Fig. 2

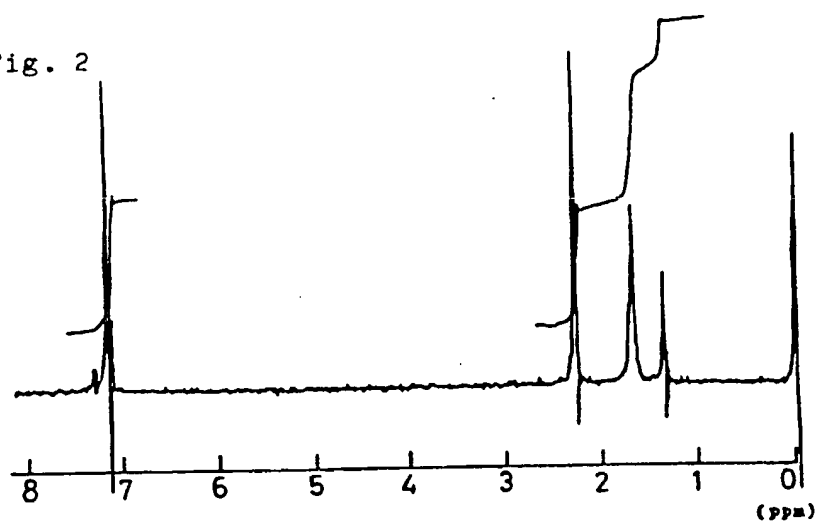


Fig. 4

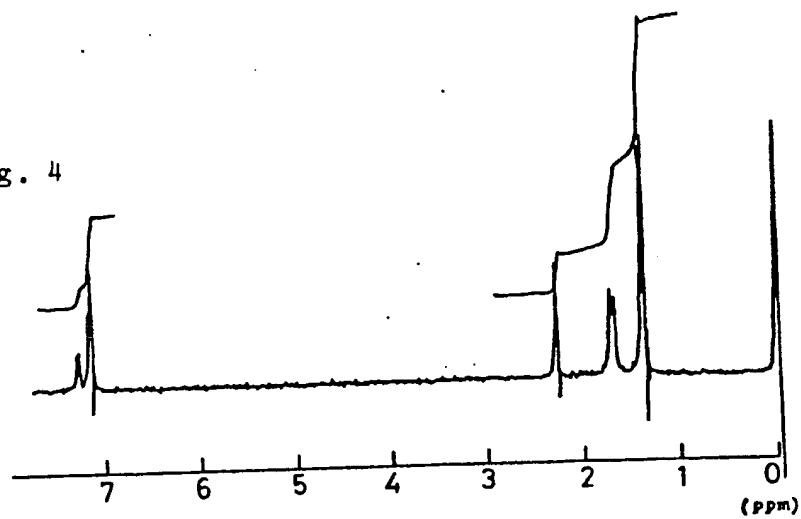


Fig. 6

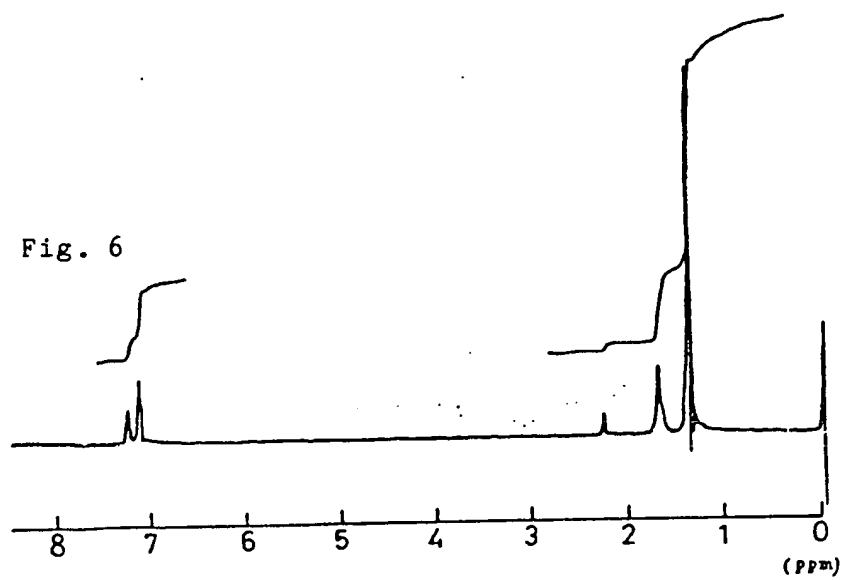


Fig. 7

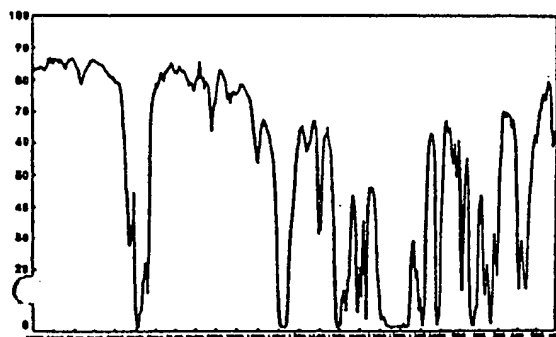


Fig. 8

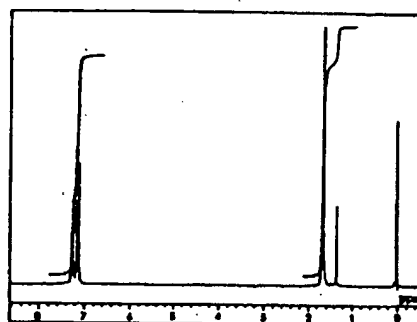


Fig. 9

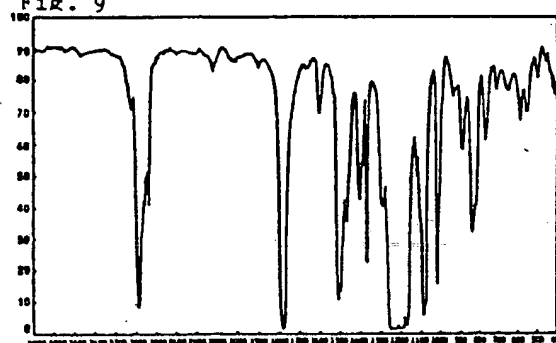


Fig. 10

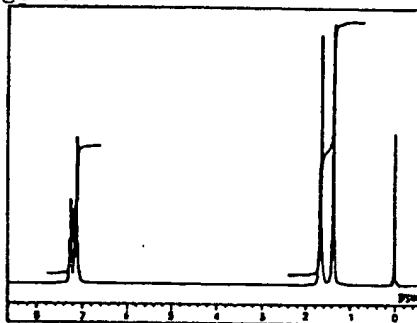


Fig. 11

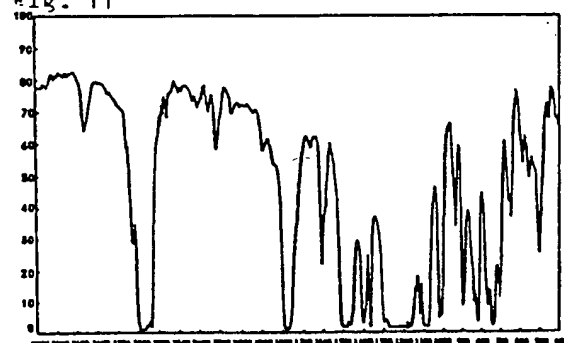


Fig. 12

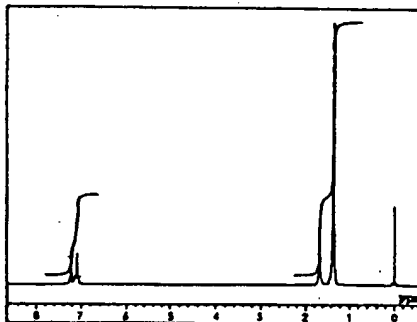


Fig. 13

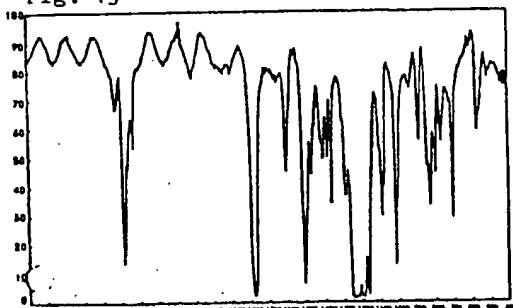


Fig. 15

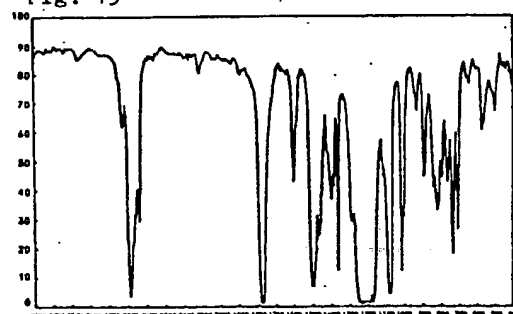


Fig. 17

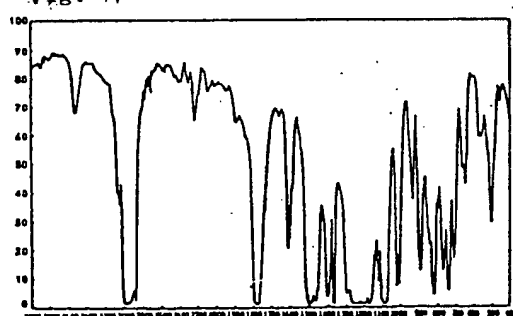


Fig. 14

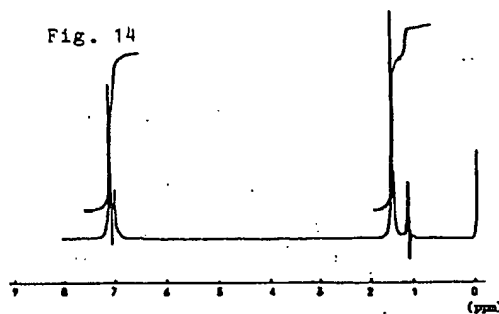


Fig. 16

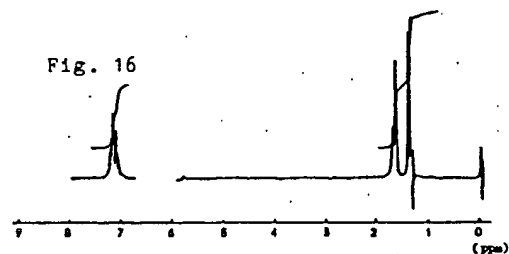


Fig. 18

